

REPORT DOCUMENTATION PAGE

Form Approved
OMB NO. 0704-0188

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1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE 10/31/96	3. REPORT TYPE AND DATES COVERED Final Progress (04/01/93-07/31/96)
4. TITLE AND SUBTITLE Deformation and Fracture Behavior of Molecular Composites Via Ionic Interactions		5. FUNDING NUMBERS DAAH04-93-G-0086
6. AUTHOR(S) Masanori Hara		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Rutgers, The State University of New Jersey Department of Mechanics and Materials Science College of Engineering Piscataway, NJ 08855-0909		8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211		10. SPONSORING / MONITORING AGENCY REPORT NUMBER AR030890.16-MS
11. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.		
12a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited.		12b. DISTRIBUTION CODE 19961125 178
13. ABSTRACT (Maximum 200 words) Melt-processable <i>molecular composites</i> have been developed and their mechanical behavior has been investigated. In these composites, rigid-rod molecules, which serve as a reinforcer, are well dispersed in a flexible-coil matrix polymer due to strong <i>ionic interactions</i> between the components. In this new type of composite material, mechanical properties are effectively enhanced by a very small addition (several %) of reinforcers. As a reinforcer, we have prepared PPTA (or Kevlar) with various ionic groups, ion content, and counterions. The mechanical behavior of molecular composites made from an amorphous polymer is unique in that not only stiffness and strength but ductility is enhanced. This is because crazing is suppressed in favor of shear deformation due to molecular level interactions between ionic rod and coil molecules; a condition not seen for conventional macro-fiber composites. The mechanical behavior of molecular composites made from a ductile, crystalline polymer indicates that both stiffness and strength can be significantly enhanced without losing toughness upon small addition of ionic Kevlar (only several %). A most dramatic change in mechanical properties is seen for the composite made from a soft, rubbery matrix polymer. Since strong/stiff reinforcing molecules (ionic Kevlar) are dispersed, very effective reinforcement is achieved.		
14. SUBJECT TERMS Mechanical Properties, Molecular Composites Via Ionic Interactions		15. NUMBER OF PAGES 16. PRICE CODE
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED
		20. LIMITATION OF ABSTRACT UL

Deformation and Fracture Behavior of Molecular Composites via Ionic Interactions

Final Progress Report

Masanori Hara

October 30, 1996

U. S. Army Research Office

DAAH04-93-G-0086/P-30890-MS

Rutgers University

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A Statement of the Problem Studied

The overall aim of our research program is to develop melt-processable *molecular composites* and to investigate their mechanical behavior. In these composites, rigid-rod molecules, which serve as a reinforcer, are well dispersed in a flexible-coil matrix polymer due to strong *ionic interactions* between the components. In this new type of composite material, mechanical properties are effectively enhanced by a very small addition of reinforcers.

A Summary of the Most Important Results

Since technical materials were reported in the interim progress reports, only a summary of the most important results are given. We have studied the deformation/fracture behavior of the molecular composites and have found significant enhancement in the mechanical properties of the matrix polymers upon addition of small amounts (several wt%) of reinforcing polymer. As a reinforcer, we have prepared PPTA (or Kevlar) with various ionic groups, ion content, and counterions.

1. Molecular composites made of ionic Kevlar and an *amorphous polymer*

We have found that homogeneous molecular composites were successfully produced by using ionic interactions between the components and that these composites are melt-processable. We have also found that *shear deformation* is induced in the matrix polymer, poly(4-vinylpyridine)(PVP), which deforms only by *crazing* without reinforcers. Such a change usually implies an enhancement in fracture properties of polymers; e.g., 5 % addition of PPTA leads to a 70 % higher stiffness and a 46 % higher strength; and more importantly, a 200 % increase in toughness is noted. This is due to suppression of crazing in favor of shear deformation, which prevents premature failure of PVP.

These are the first cases where a deformation mode change in molecular composites has been demonstrated upon addition of rod molecules, to the best of our knowledge. We reason that these deformation mode changes are caused by an enhanced effective "entanglement" (strand) density: both ionic cross-links and physical entanglements between rod and coil molecules contribute to an increase in the strand density.

These molecular (or microscopic) level interactions between reinforcer and matrix polymer molecules is indeed characteristic to molecular composites via ionic bonds. This is in contrast to macro-fiber composites, where interactions between reinforcing fibers and matrix polymer occur only at the fiber-matrix interface during load transfer; there is no influence by fibers on the deformation mode of the matrix polymer.

2. Molecular composites made of ionic Kevlar and a *crystalline polymer*

To develop more ductile molecular composites, a crystalline polymer is used as a matrix polymer. Poly(ethylene oxide)(PEO) is chosen for that purpose. These composites show good miscibility up to 6% ionic Kevlar content.

We have found that the mechanical properties are significantly enhanced. In the molecular

composites made of low molecular weight PEO, in which large spherulites are formed, brittle fracture is noted. This is due to easy crack propagation through weak inter-spherulite boundaries. It appears that ionic Kevlar reinforces the weak boundaries and enhances the mechanical properties: for example, an addition of 2% of ionic Kevlar into PEO leads to 15% increase in stiffness; 92% increase in strength; and 300% increase in toughness. We have also observed a 100% increase in fracture toughness in PEO upon addition of 2 % ionic Kevlar.

By contrast, in the composites made of high molecular weight PEO, in which smaller spherulites are formed, ductile behavior is noted. In this case, ionic Kevlar increases both stiffness and strength by reinforcing the amorphous phase of PEO; ductility reduces moderately, but overall energy to fracture (or toughness) is slightly increased.

While the molecular composite made of a crystalline polymer is more complex than that of an amorphous polymer, this also means that there are more variables to control morphology and their mechanical properties. Therefore, there are more opportunities for tailor-making molecular composite materials with various mechanical properties, ranging from strong/brittle to ductile.

3. Molecular composites made of ionic Kevlar and an *elastomeric polymer*

Although advanced mechanical applications may not be possible, we have also made the composite made from a matrix polymer which is very soft and rubbery. For that purpose, we used poly(propylene oxide)(PPrO), which is amorphous and rubbery at ambient temperature. We have found that, due to an incorporation of a strong/stiff reinforcing polymer, Kevlar, a dramatic increase in mechanical properties is achieved: for example, upon addition of 10 % of ionic Kevlar, tensile strength increases by 600%, tensile modulus by 1100%, and toughness (which is rather large for PPrO) is unchanged. These results clearly illustrate the significant effectiveness of molecular reinforcement by ionic Kevlar.

4. High Kevlar composites

As an extension of the molecular composite work, we have also developed composites in which a high percentage of (ionic) Kevlar molecules are incorporated, for example, 80-95 %. We have found that, although Kevlar itself is not melt-processable, when ionic Kevlar is mixed with PVP that has a relatively low softening temperature (160 °C), the resulting material can be compression molded into three-dimensional structures. This is because ionic Kevlar is compatible with and dispersed in PVP that can soften and flow by heating, making the entire material processable under heat and pressure. Obviously, an unmodified Kevlar/PVP blend is not melt-processable: a mixed sample remains a powder even after applying heat and pressure. Therefore, ionic modification of Kevlar and resulting compatibility with a melt-processable thermoplastic polymer (e.g., PVP) are the key to the success of fabricating Kevlar-rich materials into three-dimensional structures. This is interesting because Kevlar is not melt-processable and only made in fiber/film forms. If melt-processable Kevlar is realized, various applications in three-dimensional forms will be possible.

Overall

The mechanical behavior of molecular composites made from an amorphous polymer is unique in that not only stiffness and strength but ductility is enhanced. This is because crazing is suppressed in

favor of shear deformation due to molecular level interactions between ionic rod and coil molecules; a condition not seen for conventional macro-fiber composites. The mechanical behavior of molecular composites made from a ductile, crystalline polymer indicates that both stiffness and strength can be significantly enhanced without losing toughness upon small addition of ionic Kevlar (only several %). A most dramatic change in mechanical properties is seen for the composite made from a soft, rubbery matrix polymer. Since strong/stiff reinforcing molecules (ionic Kevlar) are dispersed, very effective reinforcement is achieved.

Our work has clearly demonstrated the usefulness of *ionic interactions* in creating molecular composites. Many engineering polymers are polar polymers having ionic dipoles, thus, many molecular composites can be created by combining ionic Kevlar with various polar polymers. In addition, since these molecular composite materials are *melt-processable*, unlike most molecular composites developed elsewhere to date, conventional methods, such as injection molding, can be used to mass-produce these materials, therefore, the technological impact could be significant.

A List of All Publications

1. "Tensile Fracture Properties of Sulfonated Polystyrene Ionomers: 1. Effect of Ion Content," *Macromolecules*, 27, 1407-1412 (1994), with M. Bellinger and J.A. Sauer.
2. "Mechanical Properties of Ionomers," *J. Macromol. Sci., Rev. Macromol. Chem. Phys.*, C34, 325-373 (1994), with J.A. Sauer.
3. "Tensile Fracture Properties of the Blends of Sulfonated Polystyrene Ionomer with Polystyrene," *Macromolecules*, 27, 6147-6155 (1994), with M. Bellinger and J.A. Sauer.
4. "Deformation and Fracture Behavior of Sulfonated Polystyrene Ionomers: Effects of Counterion and Excess Neutralizing Agent," *Polymer*, 35, 5478-5482 (1994), with M. Bellinger and J.A. Sauer.
5. "Morphology and Deformation/Fracture Behavior of PMMA Ionomers and Their Blends," *Proceedings of 9th International Conference on Deformation, Yield, and Fracture of Polymers*, Paper No. P12 (1994), with X. Ma and J.A. Sauer.
6. "Poly(methyl methacrylate) based Ionomers: 1. Dynamic Mechanical Properties and Morphology," *Macromolecules*, 28, 3953-3962 (1995), with X. Ma and J.A. Sauer.
7. "Poly(methyl methacrylate) Ionomers: 2. Deformation Behavior," *Macromolecules*, 28, 5526-5534 (1995), with X. Ma and J.A. Sauer.
8. "Molecular Composites via Ionic Interactions and Their Deformation/Fracture Properties," *Polym. Mater. Sci. Eng.*, 72, 544 (1995), G. Parker, W. Chen, and M. Hara.
9. "Molecular Composites via Ionic Interactions and Their Deformation/Fracture Properties," *ACS Symp. Ser.*, 632, 54-68 (1996), with G. Parker, W. Chen and L. Tsou.
10. "Molecular Composites via Ion-Dipole Interactions: PPTA Anion/PEO System," *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, 37(1), 390-393 (1996), with L. Tsou.

11. "Ionic PPTA's and Their Molecular Composites with Amorphous Polar Polymers," *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, 37(1), 388-391 (1996), with W. Chen.
12. "Mechanical Properties of Ionomers," in *The Polymeric Materials Encyclopedia: Synthesis, Properties, and Applications*, J.C. Salamone ed., CRC Press, Boca Raton, Florida, vol.5, p.3465-3473 (1996), with J.A. Sauer.
13. "Deformation Modes and Dynamic Mechanical Properties of Poly(styrene-co-sodium Methacrylate) Ionomers," *Polymer*, 37, 4739-4745 (1996), with X. Ma and J.A. Sauer.
14. "Fatigue Behavior of Sulfonated Polystyrene Ionomers and Their Blends with Polystyrene," *Polymer*, in press, with M. Bellinger and J.A. Sauer.
15. "Poly(p-phenylene terephthalamide)(PPTA) having Ionic and Nonionic Side Groups and Its Blend with Poly(4-vinylpyridine)," *Polymer*, in press, with G. Parker.
16. "Molecular Composites via Ionic Interactions: 1. Miscibility of PPTA Polyanion and Polyvinylpyridines via Ion-Dipole Interactions," *Polymer*, in press, with G. Parker.
17. "Mechanical Properties of Ionomers and Ionomer Blends," in *Encyclopedia of Polymer Processing Technology*, N.P. Cheremisinoff ed., Marcel Dekker, New York, in press, with J.A. Sauer.

A List of All Participating Scientific Personnel

Dr. Masanori Hara

Dr. John A. Sauer

Gary Kupperblatt (earned Ph.D. degree during the period)

Greg Parker (earned M.S. degree during the period)

Li-Chun Tsou

Weng-Chao Chen

Technology Transfer

Contacts with the following institutions were made. Names and telephone numbers of the people contacted are shown.

- Army Laboratories, Picatinny Arsenal: Dr. D. Wiegand, (201) 724-3336
- Hoechst-Celanese: Dr. H.H. Yoon, (908) 522-7786

The PI attended and presented papers at various meetings and organizations. A list of presentations is shown below:

1. "Mechanical Properties of PMMA Ionomers and PMMA Ionomer Blends," at Rohm & Haas, July 1993.
2. "Morphology and Deformation/Fracture Behavior of PMMA Ionomers and Their Blends," at 9th International Conference on Deformation, Yield and Fracture of Polymers, Cambridge, Apr. 1994.
3. "Deformation and Fracture Behavior of Ionomers and Ionomer Blends," at Hoechst Celanese, Apr. 1994.
4. "Development of Molecular Composites via Ionic Interactions," at Hoechst Celanese, Nov. 1994.
5. "Molecular Composites via Ionic Interactions and Their Deformation/Fracture Properties," at the Symposium on "Processing-Structure-Property Relationships in Liquid Crystalline Polymers," American Chemical Society National Meeting, Anaheim, April 1995.
6. "Ionic Interactions in Polymeric Materials and Hierarchical Structures," ARO Workshop on "Hierarchical structures," South Carolina, May 1995.
7. "Molecular Composites via Ionic Interactions and Their Deformation/Fracture Behavior," Gordon Research Conference on "Ion-Containing Polymers," New Hampshire, July 1995.
8. "Development of Ionic Liquid Crystalline Polymers and Their Blends (Composites)," Senior Technical Staff Meeting, Hoechst-Celanese, September 1995.
9. "Ionic PPTAs and Their Molecular Composites with Amorphous Polar Polymers," Symposium on "Ionomer Blends and Complexes," at the ACS National Meeting, New Orleans, March 1996.
10. "Molecular Composites via Ion-Dipole Interactions: PPTA Anion/PEO System," Symposium on "Ionomer Blends and Complexes," at the ACS National Meeting, New Orleans, March 1996.